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**A Study of the Formation
of Cuprous Oxide in Glazes**

Ceramic Engineering

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**A STUDY OF THE FORMATION
OF CUPROUS OXIDE IN GLAZES**

BY

OTTO SPRINGE

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CERAMIC ENGINEERING

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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May 24th 1962.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Mr. Otto Springe

ENTITLED

A Study of the Formation of
Cuprous Oxide in Glazes

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

B. S. in Ceramic Engineering

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Instructor in Charge

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HEAD OF DEPARTMENT OF

Ceramics.



A STUDY OF THE FORMATION OF CUPROUS OXIDE IN GLAZES.

The use of copper oxide for the production of red ceramic colors probably was first found in the manufacture of glass. According to our knowledge of antiquity, opaque red glasses; which contain copper as a coloring agent have been found. The first authentic communications of its use, date back to the time of Plinius and Hiraklius; the latter also discovering that if copper filings, that being the form in which it was first attempted to be used, were heated to a glowing temperature, a black powder, copper oxide; was formed.¹ In these communications no mention is made of red color resulting from its use and the coloring effected by copper here referred to is probably the characteristic greenish blue produced by the cupric oxide. The afore mentioned opaque red glasses of antiquity; were probably more the product of chance than of definite aim.

The ruby glass which was produced at the beginning of the 17th century soon became a lost art; and the colors produced thru copper were considered to be from gold until this erroneous idea was corrected by the chemical analyses of Klapproth and D'Arcet. This lead to the keen investigation and researches of many scientists; and it was found that the red color produced in ruby glass was due to the lower oxide of copper. This probably is formed from the cupric silicate forming cuprous silicate. From this, colloidal cuprous oxide segregates out under proper heat treatment.²

¹Die Glas-Fabrikation. - Gerner.

²Dralle - Die Glasfabrikation. Vol. 1. 130.

Engelhardt in 1826 investigating the above named changes proved that in order to convert the cupric oxide to cuprous oxide some reducing agent as tin and tartaric acid had to be added to the glass batch.¹ His investigation showed that for 100 parts by weight of glass batch, 2 parts of cuprous oxide and $1\frac{1}{2}$ parts of stannous oxide were sufficient to impart to the glass a ruby red color. To prevent this from again changing to the green he conceived the idea of adding some tartaric acid as a reducing agent. He also maintained that lead glasses were most easily changed to the red color and that these required the smallest amount of coloring agent, although in these statements he was contradicted by many of the other authors. His work was corroborated by that of Bontemps who at this same time was carrying on investigations on these same lines in France.

In 1847 Pettenkofer,² while attempting to determine the chemical changes that took place in the glass melt causing the color to change from green to red, discovered "Hamatinon", an opaque rich red glass which was remarkable for its crystalline structure. The batch used by him was as follows:

100	parts	by	weight	of	Sand.
50	"	"	"	"	Soda.
11	"	"	"	"	Lime.
1	"	"	"	"	Magnesia.
33	"	"	"	"	Red Lead.

This was molten into a clear mass to which 20 parts of copper scale (cuprous oxide) and 3 parts of iron scale (iron oxide)

¹Die Glas-Fabrikation. - Gerner.

²Mertens Glas - Fabrikation.

were added and later a small quantity of charcoal. The glass was then blown several times in order to thoroughly mix the color ingredients with the melt. The temperature of the furnace is then reduced and the glass melt allowed to take a more viscous form, which heat is maintained for about 10 hours.

The glass formulas used today do not differ very materially from those used by Ebell and Pettenkofer; in place of copper scale cuprous oxide is used and as a reducing medium tin oxide. Two of the glass batches in use today are as follows:¹

100 kg.	Sand	100 kg.	Sand
20 "	Molasses	20 "	Saltpeter
12 "	Red Lead	18 "	Borax
10 "	Borax	30 "	Lead Oxide
4 "	Cuprous Oxide	3 "	Cuprous Oxide
3 "	Tin Oxide	1 "	Tin Oxide
0.5 "	Iron Oxide	2 "	Manganese Dioxide
1. "	Manganese Dioxide.		

According to German practice the batch is put into the furnace and heated for 5 to 6 hours, during which time it is blown several times, then drawn and run into cold water washed and re-melted. The above operation is repeated several times thus purifying the melt.

The earliest use of copper to produce red color in glazes is found on old Chinese porcelain; which glaze on account of its particular color is called Chinese red or ox blood.²

¹Mertens Glas - Fabrikation.

²Seeger. Collected Works Vol.II. pp. 734.

Messrs. Lauth and Dutailly published an extensive treatise on the character of the color of this glaze in which they described the the method used by them in its production. In this treatise these investigators formerly active in the factory at Sevres proved that this color can be imparted only only to a body which requires a lower finishing temperature than that which is necessary for European porcelain. The porcelain used by them was like the Chinese, one containing very much silica, and which hence vitrifies easily a body which is now made quite extensively at Sevres, the glost temperature of which is stated as being 1300°C. They said that the red color of the glaze is produced in the presence of tin oxide by a violent process of reduction, to which the ware is exposed in burning. The copper oxide is reduced to metallic copper, this being dissolved in the glaze and imparting to it on slow cooling a copper red color while on more rapid cooling a colorless glaze is produced which however, becomes red on gradual heating.

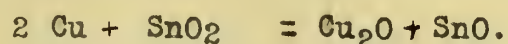
Copper red glazes were first produced on a larger commercial scale in Europe by Seger,¹ who while at the Royal Porcelain Factory in 1879 carried on extensive investigations along this line. Seger² in summarizing the results of his investigations, says, "I cannot agree with the opinion of the above named investigators, (Lauth and Dutailly) regarding the production of the red color by a segregation of metallic copper from the glaze that is, by a simple and strongly reducing, firing condition."

¹Thonind. Ztg. 1883, No.7.

²Collected Works, Vol. II, pgs. 734 to 750.

He says; "On the contrary alternately reducing and oxidizing conditions of the fire gases are required to produce it, and the difficulties of manufacture lie less in the composition of the glaze itself than in the proper constitution of the fire-gases. It was shown in the production of the red color, that in using one and the same glaze, not only variations in shade from black thru brown to sealing-wax red and light bluish green are produced in the same burn, but, that some pieces are colored different on one side than the other; according to the intensity of draft thru the piles of saggars. Some burns may produce in the same glaze a more or less beautiful color than others, and again some firings may be totally spoiled and not produce any red color at all, everything appearing gray or black.

The object of the oxidizing agents added to the glaze, is to convert the black metallic copper to a cuprous silicate, and this imparts to the glaze a red color, the ingredients according to Seger reacting as follows:



The best results are obtained by reducing with hydrogen and carbon monoxide; for if illuminating gas is used for this purpose a part of its carbon is deposited, owing to the decomposition of the gas, which surrounds the glaze particles and thus prevents fusion.

The glaze thus becomes less fusible and retains its porous character even temperatures above its melting point. If glazes reduced in this manner are heated in air, the carbon is burned out, and at the same time the copper segregated out is also oxidized to cuprous oxide and the glaze fuses to a red colored glaze.

Heubach¹ found that copper red glazes develop best between cone 5 and cone 7, in agreement with Seger. The glazes must be fired in a reducing atmosphere but if over reduced they turn brown mingled with metallic spots. The glazes should be fusible, rich in alkalies and must contain but little copper oxide. Seger obtained good results with 10% to .15% for dark red and 0.5% to 1.0% for lighter tints. Seger explains this fact as follows: In glazes with a small content of copper, the resulting cuprous oxide is completely dissolved in the glaze. Consequently the glaze becomes transparent and makes the color appear darker and more beautiful, while a greater amount of copper renders the glazes opaque and lighter tinted.

The object of this investigation was to determine, first the critical temperature necessary to bring about the change from the green cupric to the red cuprous oxide, second, after having determined this point to study the methods which could be employed to produce sufficient reduction without harming the glaze and thus bring about the desired change.

Three types of glazes were experimented upon.

(a) Alkaline Glaze.

.4 Na ₂ O		
.55 CaO	0.2 Al ₂ O ₃	2.SiO ₂
.05 CuO		0.05SnO ₂

(b) Whiteware type.

0.35 Na ₂ O		
.60 CaO	0.3Al ₂ O ₃	3.SiO ₂
.05 CuO	0.15B ₂ O ₃	0.05SnO ₂

(c) Porcelain type.

.30 K_2O		4 SiO_2
.65 CaO	0.4 Al_2O_3	0.05 SnO_2
.05 CuO		

Glazes a and b were all fritted with the exception of .1 equivalent and .15 equivalent of kaolin respectively.

The preliminary experiments were made with the glazes contained in small porcelain boats inserted in a fused quartz combustion tube. Later the glazes were tested on porcelain discs made on the jigger wheel, and vases cast in plaster molds.

The porcelain body batch had to be one which could be used in casting, jiggering and pressing. A body which met these requirements was of the following composition.

Tennessee Ball Clay #7 = 20

Georgia Kaolin = 10

North Carolina Kaolin = 10

English Ching Clay #7 = 10

Feldspar (potash spar.) = 20

Flint (Ohio 8 hr. grind) = 30

For casting $\frac{1}{2}\%$ $Na_2 CO_3$ was added.

This body vitrified at Cone 9.

Method of Preparing Glazes.

The fritts for glazes (a) and (b) were fused in a drip fritt crucible. The fritt was then ground dry in a porcelain ball mill; until it passed the 100 mesh sieve. Then the required amount of kaolin to complete the glaze batch was added and the glazes were ground wet in ball mill for about two hours and screen-

ed thru an 80 mesh sieve. Glaze (c) being a porcelain glaze did not require any fritting; its batch was weighed up ground for two hours in a porcelain ball mill and screened thru the 80 mesh sieve. All glazes were set at the same density which was 1560 degrees on the scale of the B and L hydrometer.

Determination of the Critical Temperature.

To determine the critical temperature, or that temperature, at which the green cupric silicate glaze changes to the red cuprous glaze ^{when} fired under reducing conditions, a Hoskins electric combustion furnace was employed. The apparatus as set for this purpose is illustrated in fig. 1.

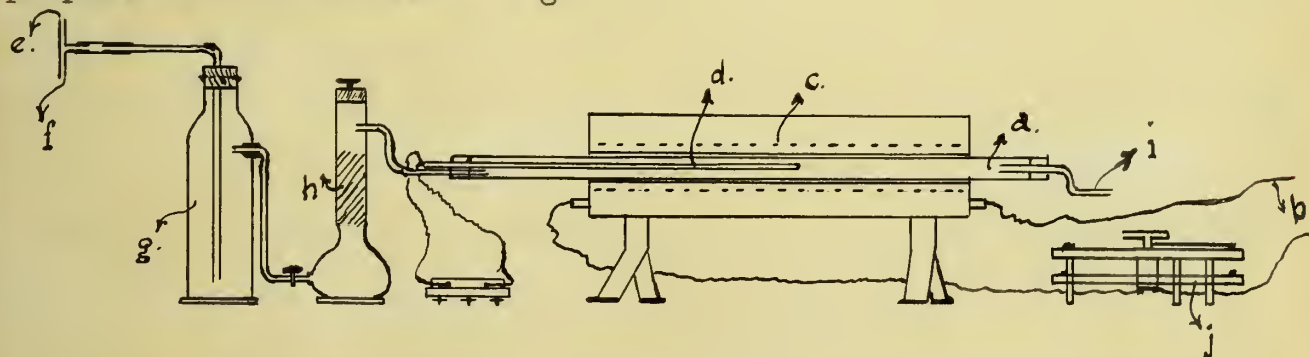


Fig. #1.

- | | |
|-----------------------------|--|
| (a) Quartz combustion tube. | (g) KOH solution to remove CO_2 from the gas. |
| (b) Electric leads. | (h) CaCl_2 to remove H_2O . |
| (c) Platinum heating coils. | (i) Tube at which gas is burned. |
| (d) Thermo couple. | (j) = Rheostat. |
| (e) Gas lead. | |
| (f) Air lead. | |

The change from reducing to oxidizing conditions can be

rapidly made by using a T.tube one end of which is connected to the gas and the other to a compressed air lead. The glazes were put in porcelain boats, which were made by pressing in plaster molds. The dimensions of the boats after burning were $7/8$ inch long, $9/16$ inch wide and $5/32$ inch deep. The boats were biscuit-fired in a gas fired furnace, then the glazes were put in these and fired in the furnace under oxidizing conditions. The alkali glaze was of a fairly good green color but was crazed, it had more life and lustre than glazes b and c. Both b and c were of pale green color probably due to too thin dipping.

Illuminating gas was used as a reducing agent and since this would carbonize the couple inserted in the furnace, some way to protect the thermo couple had to be devised. This was done by inserting the couple into a closed quartz tube which was $12\frac{1}{2}$ inches long and $1/8$ inch bore, the wires being insulated from each other by asbestos. Since the couple used for this experiment was old and had several welds; it was first calibrated against a standard couple. The trials were placed in the tube of the furnace, and heated to different temperatures at different rates, starting reduction at 650°C and alternating from reducing to oxidizing conditions every 13 minutes, firing 3 minutes oxidizing and 10 minutes reducing.

Result of Electric Furnace Firings.

Of about 20 furnace runs; the best results, that is the best red colors were obtained from glazes b and c. These seem to be most easily changed from green to red and produced the

red color most consistently. The critical temperature is between 950°C and 1000°C , although the change can be produced at lower temperatures if fired reducing for a longer period of time. In this series of experiments, under these particular conditions the schedule for the best results was as follows: Glazes were good green color when put into the furnace. The firing was carried to a temperature of 800°C . under oxidizing conditions, then from 800°C to 875°C (time 15 min.) reduction was maintained. Oxidizing conditions were then caused to prevail for 5 min. and from 890°C to 940°C . (time 15 min.) reduction. Beginning from this point air was admitted until 975°C . which was the finishing temperature of the burn. The object of finishing the burn under oxidizing conditions is to burn off any free carbon that may have been deposited on the trials. The results of these firings are compiled in the following tabulation.

Duration of Reduction	Tempature of reduc- tion C.	Finishing Temp. C.	Glaze	Color
20 minutes	600-750 805-850	850	A	Red around edges and in craze marks
40 minutes	500-600 700-780 845-930	950	A	Color is red but glaze is blistered.
1 hour 7 minutes	550-670 700-780 850-915	1000	A	Dark red of in- tense metallic lustre.
45 minutes	650-750 800-875 930-940	975°C	B.	Blood red
45 minutes	650-750 800-875 930-940	975	C	Good red.
40 minutes	600-700 770-800 850-930	1000	B.	Pale red, small spots of green.
40 minutes	600-700 770-800 850-930	1000	C.	Good red.

The next step was an attempt to produce these results in a larger gas fired test kiln. The kiln used for this purpose was the Seger-Heinecke laboratory test kiln, fired with illuminating gas. The glazes to be tested in this kiln were dipped on porcelain discs 1 7/8 inch in diameter, and fired in a gas fired furnace under oxidizing conditions. All glazes were green, the

alkali glaze having the darkest shade and best lustre, but was slightly crazed; b and c had a pale green shade. the trials were set in the muffle of the Seger kiln, one trial of each type to to a burn. The object of this experiment was finding if possible some way of adding a reducing agent other than gas to cause the reaction. The reducing agents introduced into the muffle were coke, resin, cylinder oil, machine oil, and petroleum. Of these petroleum worked most successfully. The firing was governed by the schedule determined by the electric furnace runs slight changes being made to suit the particular reducing agent used. Results of burns:

Although some red colors were obtained the majority of trials were black and pitted. The glazes lacked life and lustre, which is probably due to the deposition of carbon, which in a closed muffle as this furnace was has no opportunity to burn out completely, thus making the glaze less fusible. It was found that the oils gave ^{the} best results, and of these, the most volatile ones which form vapors coming in direct contact with the glaze. The great difficulty in this particular furnace was to get the oil down into the muffle before it volatilizes in the tube. This was done by inserting a fire clay tube thru the 7/8 inch hole in the lid, the bore of the tube was $\frac{1}{2}$ inch, length 2 ft. At the top of the tube a separatory funnel is sealed into which the oil is put. Thru the smaller perforation in the lid the thermo couple tube is inserted and temperatures read from a galvanometer. The apparatus as set up for use is shown in figure #2.



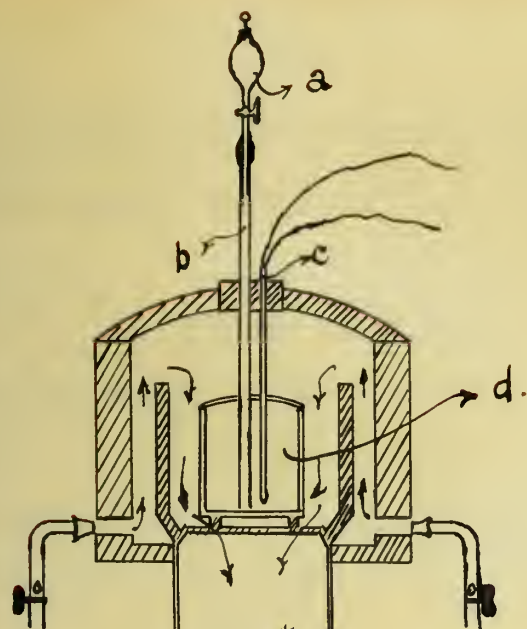


Fig. # 2.

- a. Separatory funnel.
- b. Fire clay tube.
- c. Quartz thermo couple tube.
- d. Muffle.

Part of the oil decomposes in the tube; and after two or three burns the bore of the tube becomes choked with a hard deposit of carbon, thus preventing the oil dropping into the muffle.

The porcelain glaze gave the best results as to color, both the alkali and whiteware glaze are easily over reduced and remain black, although in respect to gloss these are better. The glazes were fired alternately oxidizing and reducing.

Schedule.

Burn oxidizing to 900°C.

900 to 980°C, 15 minutes reducing, followed by 10 minutes oxidizing.

1010 to 1070°C, 20 minutes reducing, finish burn, oxidizing for 15 minutes, at 1100°C.

Since the results of the burn are entirely dependent upon the kiln conditions; these must be such that they can easily be controlled and regulated by the burner. To make this possible the reducing agent should be in form of a gas, and it was with this aim in view that the next attempts to fire the glazes

in a larger gas fired kiln, in which gas could be used as a reducing agent, were made.

Series I.

The object of further experiments was to determine the best amount of copper oxide to use in order to obtain a good red color. The base of the series was a porcelain glaze practically the same formula as glaze c. The series is formed by blending the two end glazes.

Glaze A. .

.3 K_2O 4. SiO_2
 0.4 Al_2O_3 0.05 SnO_2
 .7 CaO

Glaze B.

.3 K_2O 4. SiO_2
 .6 CaO 0.4 Al_2O_3 0.05 SnO_2
 .1 CuO

Nos. 1 2 3 4 5 6 7 8 9 10 11

Glaze A.	10	9	8	7	6	5	4	3	2	1	
		1	2	3	4	5	6	7	8	9	10
											Glaze B.

The glazes were blended by weight according to above table. After grinding and screening the glazes were set at 1560 degrees on the scale of the B and L hydrometer. They were applied on biscuited porcelain discs by dipping and fired in the gas furnace. The temperature to which they were carried was 1250°C. A series was obtained that shaded down from a dark green to a white glaze. The series of discs was again set in the gas

furnace, together with a trial of glaze b. The furnace was heated under oxidizing conditions to a temperature of 940°C. From this point on it was fired alternately reducing and oxidizing, for 10 and 5 minute intervals respectively, for a total time of 3 hours and 50 minutes.

Results of the burn.

After firing 30 minutes under reducing conditions, the trial of glaze b. was drawn, the temperature now was 1040°C. The trial was a good bright red color, of slight metallic lustre and the color in the glaze appeared curdled. The red color attained in this series was only of slight strength. It did not begin to show until trial 7 was reached. From here on to trial 11 it became stronger, No. 11 being the darkest. This difficulty seems to be due to the fact that the color is lost after having once obtained it due to heating at a high temperature in trying to mature the glaze. To overcome this difficulty another series was run to get a glaze which would mature at a lower temperature. Such a glaze should have more lustre and life; and according to trial (b) drawn after reducing 30 minutes should develop the red color more easily. Since this furnace is fired by two air blast gas burner, it is easily changed from oxidizing to reducing conditions or vice versa, by regulation of the air and gas valves.

Series II.

In order to develop a glaze with a lower maturing temperature, a series was run between two glazes of wide difference in maturing temperature. One of these was a glaze con-

taining borax and required fritting, the other a glaze of the porcelain type.

Glaze C, matures at Cone 6 or 7.

.3K₂O
 .44 CaO 3.2 SiO₂
 .4Al₂O₃ 0.05 SnO₂
 .2 BaO
 .06 CuO

Glaze D, develops best between cone .02 and 01.

.25 K₂O
 .30 CaO .35 Al₂O₃ 3.2 SiO₂
 .15 BaO .5 B₂O₃ .05 SnO₂
 .25 Na₂O
 .05 CuO

In above glaze all but .08 equivalent ball clay was fritted.

After grinding and screening they were blended according to the following proportions, by weight.

Nos.	1	2	3	4	5	6	7	8	9	10	11
Glaze C	10	9	8	7	6	5	4	3	2	1	
		1	2	3	4	5	6	7	8	9	10

Glaze D.

These glazes were dipped on biscuited porcelain trial discs, and fired in the gas fired test kiln. In this series it was attempted to develop the red color in one burn. The burn was completed in 8½ hours, the temperature to which the firing was carried was 1230°C. The firing conditions were oxidizing

up to 950°C; from this point on they were slightly reducing, to a temperature of 1070°C reached in $1\frac{3}{4}$ hours. The burn was finished with an oxidizing atmosphere. Towards the end of the burn all openings were stopped up so as to soak the heat thru the furnace, and to cool the glazes slowly.

Results of burn.

The high boric acid glazes were the best in respect to gloss, but showed a tendency towards crazing. All glazes were matured and of a rich deep maroon color. Some showed a very peculiar curdled effect which seemed to be most prominent in the high alkali glazes. Glazes #1, 2, 3 and 4 were of a deep cherry red color. In glazes # 5, 6 and 7 the mottled or curdled effect was most pronounced; Nos. 8, 9, 10 and 11 possessed a good dark red color, #8 being about the best glaze in respect to gloss and texture, of the entire series. In this burn an odd effect was obtained on a trial dipped with glaze a. The glaze was matt in texture probably due to overfiring, but showed an alligatorskin effect, with large spots in red and the intermediate dividing lines in deep green.

Series III.

Since the glazes of series II were of a dark maroon color it was next attempted to produce lighter red shades by blending these glazes with a glaze free from copper oxide. The glaze chosen for this purpose corresponded to the following formula.

Glaze E, maturing at cone 6 or 7.

.3 K_2O		3.2 SiO_2
.5 CaO	.4 Al_2O_3	.05 SnO_2
.2 BaO		

The ground and screened glaze slip was blended, by weight, with the glazes of Series #II, in the following manner.

1		2	
#1. 40 parts #11	10 parts E	30 parts #11 to 20 parts E	
#2. 40 "	#10 to 10 parts E	30 " #10 " " " "	
#3. 40 "	9 " " " " "	30 " # 9 " " " "	

3

20 parts #11 to 30 E
20 " #10 " "
20 " # 9 " "

In this way 33 different glazes were formed from the 11 glazes of series #II. These were dipped on biscuited porcelain discs, two trials of each glaze. The object of dipping two series being to fire one in a single fire, and the other is a double burn. The one fire glaze trials varied in color from light red thru dark red into black. In the black trials the color was intermingled with green. The second series was first^{fired} under oxidizing conditions, to a temperature of $1235^{\circ}C$ in $3\frac{1}{2}$ hours. After the series had been burned to a green glaze, the reducing burn was started, the burning schedule being as follows:

Time and temperature of reducing periods.

8.15	temperature	840°C	to	8.32	temperature	835°C
8.45	"	900°C	"	9.00	"	880°C
9.20	"	940°C	"	9.35	"	910°C
9.45	"	950°C	"	10.05	"	920°C
10.30	"	1020°C	"	10.55	"	1000°C

The burn was completed at 11:10 at a temperature of 1060°C under oxidizing conditions.

Results of burn.

The glazes of this second burn of series III possessed a better color and texture than any others obtained, the best reds were those of the glazes between, Nos. 5 and 9. Those high in in porcelain glaze were a paler liver red, while those higher in B_2O_3 were crazed. The #3 glazes of each series or those highest in clear glaze, i.e. lowest in CuO ; were the best shades. The B_2O_3 glazes have the most life and of the 33 glazes, glaze No. 6³ and No. 8³ were picked as the best.

Series IV.

The purpose of this series is to find the effect of of varying the content of CuO , maintaining the glaze composition constant. Two series were run, one low in B_2O_3 content and the other high. The base glazes of these series were #2 and #9 of series II.

Glaze #2.=glaze G.

.295 K ₂ O		
.426 CaO	.395 Al ₂ O ₃	3.2 SiO ₂
.195 BaO	.05 B ₂ O ₃	.05 SnO ₂
.059 CuO		
.025 Na ₂ O		

Glaze #9.= Glaze F.

.26 K ₂ O		
.328 CaO	.352 Al ₂ O ₃	3.2 SiO ₂
.16 BaO	.4 B ₂ O ₃	.05 SnO ₂
.2 Na ₂ O		
.052 CuO		

These two glazes were blended by weight with two other of their same formula which contained no copper. Thus the formulas of all glazes in this series, remained practically the same the copper content decreasing.

Result of burn.

The color of glaze F series, was dark; the glazes curdled and showed a tendency towards crazing. In the glaze G series better reds were developed the deepest and brightest being a glaze with the smallest copper content. This glaze contained 1 part of glaze 2 and 4 parts of glaze G.

Series #5.

This series was run to determine the effect of the lead in the glazes. The lead glaze chosen had the following formula:

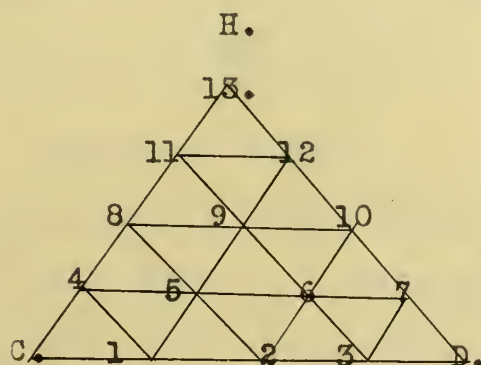
Glaze H.

.2 CaO		
.1 ZnO		
.1 MgO		1.24 SiO ₂
	.08 Al ₂ O ₃	
.5 PbO		.05 SnO ₂
.06 CuO		
.04 K ₂ O		

Fritt formula for glaze H.

.091 K ₂ O	
.227 ZnO	.114 SnO ₂
.227 MgO	1.208 SiO ₂
.455 PbO	

This glaze was blended on a triangular diagram as one of the corner glazes, the other two corners being C and D.



The corner glazes were weighed up dry, ground wet in a porcelain ball mill and blended by weight. They were then dipped on

biscuited porcelain discs and burned in the gas fired furnace under oxidizing conditions to a temperature of 1230°C. The reducing burn was carried on under the following schedule; which was found to be the most satisfactory in producing the red colors.

Temperature and time of reducing periods.

830°C to 920°C = 20 min.

928°C to 880°C = 32 min.

985°C to 880°C = 20 min.

1000°C to 920°C = 20 min.

1040°C to 940°C = 30 min.

1040°C to 980°C = 20 min.

1050°C to 950°C = 20 min.

1060°C to 1050°C = 10 min.

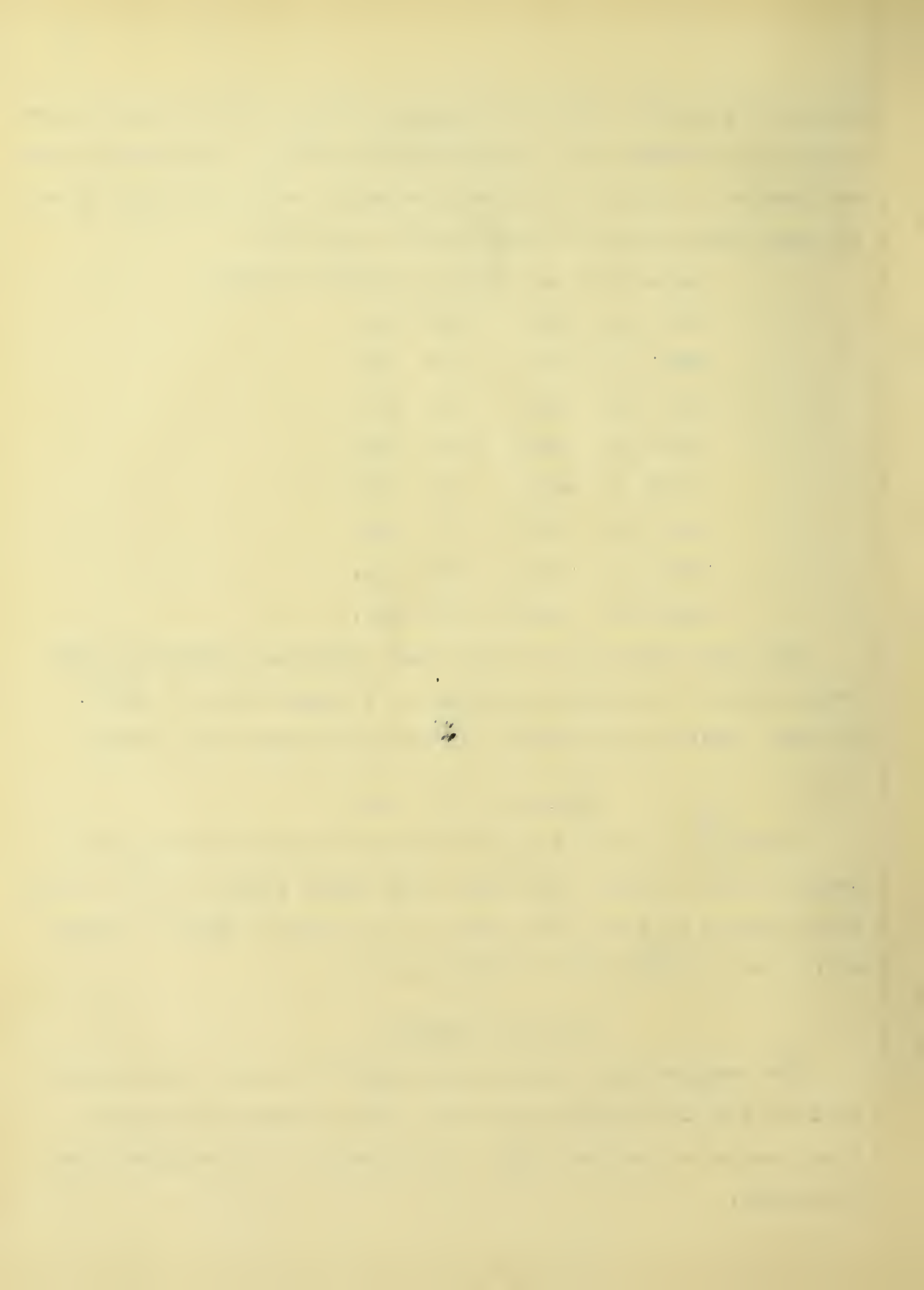
The burn should be finished under oxidizing conditions these being held for at least 10 minutes, at a temperature of 1100°C. The best results are obtained by letting the glaze cool slowly.

Results of this burn.

Glazes 9, 10, 11, 12 and 13 were dark in color showing only spots of red, and were over fired. The other glazes of this series are of fairly good red color: Nos. 4 and 8 show a metallic lustre, while the others ^{have} a decided curdled effect.

Summary of Results.

The best and most reliable glazes of all series experimented with are #6³ and #8³ of series III. These glazes when properly fired produce a good red color. The formulas of these glazes are as follows.



Glaze 6³.

.29 K ₂ O		
.448 CaO	.39 Al ₂ O ₃	3.2 SiO ₂
.19 BaO	.1 B ₂ O ₃	.05 SnO ₂
.05 Na ₂ O		
.022 CuO		

Glaze 8³.

.286 K ₂ O		
.437 CaO	.386 Al ₂ O ₃	3.2 SiO ₂
.186 BaO	.14 B ₂ O ₃	.05 SnO ₂
.07 Na ₂ O		
.021 CuO		

The above glazes develop best between cones 5 and 7. It was found that the most satisfactory results were obtained by first burning the glazes under oxidizing conditions to their maturing temperatures. Their color is then a good shade of green. The red color is then produced by refiring these according to the schedule given. The last named glazes were sprayed on some biscuited porcelain bases and fired in the gas kiln. It was found that in the same burn, the same glaze will produce different colors, depending upon the particular firing and draft conditions in the different parts of the kiln. The greatest difficulty in so small a furnace as this, is the uneven distribution of heat, causing the glaze on one side of the ware to be over burned, while on the other it may just have reached its maturing temperature.

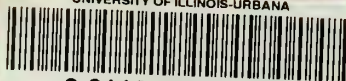
The results obtained seem to verify the statements of Seger, Heubach, and other writers, that good results depend more on the firing conditions than on the composition of the glaze. However,

it has been found that glazes containing alkalies develop a shade which has more life and lustre, although when too high in these constituents, the glazes craze easily and the color shows a tendency to become curdled. The lead glazes although of good gloss seem to be more susceptible to over reduction, in which case the color turns black. One objection to reducing with illuminating gas is the deposit of free carbon on the glaze, due to the decomposition of the gas. This causes dark spots on the glaze and makes it less fusible. To overcome this the glazes should be finished under oxidizing conditions, and if any dark irregular spots remain the glaze must be burned above its maturing temperature to overcome same.





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